



The surface hydration of soda-lime glass and its potential for historic glass dating



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ABSTRACT

More than three decades ago the idea of using ambient water diffusion on manufactured glasses as an archeological dating method was proposed for historic period artifacts. In this study, we use infrared spectroscopy (FTIR) and secondary ion mass spectrometry (SIMS) to model water diffusion into the surface of two soda-lime glasses that differ principally in the alumina and magnesium content. Lower temperature hydration experiments (60–140 °C) were conducted and the surface diffused water was measured by infrared absorption, transmittance, and reflectance spectroscopy to establish the diffusion coefficients and activation energies, and to investigate the change in glass surface structure with time at a constant temperature. SIMS was also used to document water diffusion within a sample recovered from a 19th century archeological slave quarters at Thomas Jefferson's Monticello plantation in Virginia, USA.

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1. Introduction

Archeological chronology is central to the understanding of changing human behavior and in large part relies upon dated organics and unique forms of cultural material to estimate the time and duration of human activities. In the field of historic archeology ceramics are frequently used to provide age estimates for cultural deposits of the recent past and may provide a dating resolution of just a few decades for 18th and 19th century archeological contexts. In many other situations ceramics are only very general age estimators because of their generic appearance and lengthy period of manufacture. In addition, a temporal lag between the actual age and the disposal period (Adams, 2003) can further remove the dated event, the manufacturing period, from the target event, the disposal of the artifact (Dean, 1978). Thus, any new chronometric technique that can provide an age for the disposal event in a more direct manner has a distinct advantage. For many non-heirloom glass artifacts, it is reasonable to assume that the breakage event is very close in time to the discard of the broken glass. Therefore, determining an age of fracture (breakage) would establish the time of entry into the archeological record and provide dates for human use of structures and landscapes.

We initiated a series of preliminary experiments to look at the potential of using the hydrated surfaces of historic period glasses as chronological indicators. Similar to the method of obsidian hydration dating (Friedman and Long, 1976; Stevenson and Novak, 2011), the rate of water diffusion into the glass surface is experimentally established and used to estimate the age of an artifact based upon the total diffused water under certain environmental parameters that include ground temperature (Rogers, 2007, 2008) and soil relative humidity.

American archeological glasses beginning in the 17th century originated primarily from Great Britain which capitalized on the talents of French glassmakers. One of the most notable developments of this century was a remarkable increase in the production of containers, mostly bottles, promoted by the switch from wood to coal furnace fuel that resulted in a significant cost savings (Crossley, 1998). At this time, there was no profession-wide recipe that was circulated amongst the independent glass houses. As advances in glass processing continued, so the variety of glass compositions increased. As a result, glass compositions became highly variable as producers experimented to find combinations of silica and fluxes (e.g., calcium, potassium) that resulted in a suitable product. In this preliminary study, we are not able to address all of the complex issues surrounding compositional variability and have chosen to restrict our investigations to the soda-lime-silicate glasses that were used for containers and window panes.

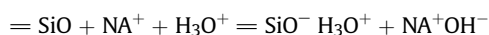
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2. Previous research

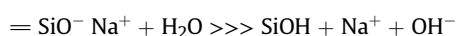
The idea of using the hydrated surface of soda-lime-silicate glass as a potential dating method was initially proposed by Lanford (1977, 1978) who used ^{15}N nuclear resonance reaction of the glass surface to record a hydrogen profile that represented the depth of water (hydrogen) diffusion. He found that water diffused into the surface of glass in a regular manner where the depth of diffusion followed the square root of time. Further investigations from an archeological dating perspective did not emerge and we are not aware of any applications of hydration dating on historic soda-lime glass artifacts, but accelerated hydration experiments with high calcium glasses (Stevenson et al., 2007) and the dating of 19th century historic contexts have given some encouraging results.

A considerable number of investigations have looked at the basic process of soda-lime-silicate glass hydration. Doremus (1975) originally proposed an ion exchange model where hydronium ions enter the glass surface and reacted with the glass network:



The model specified that H_3O^+ was the mobile water species and this was supported by the observation that the ratio of sodium to diffused hydrogen was approximately 1:3 (Lanford et al., 1979; Smets and Lommen, 1983) meaning that three hydrogen atoms replaced a single sodium atom.

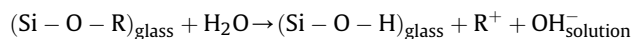
While the basic exchange process has remained accepted until the present, another exchange mechanism has been proposed by Smets and Lommen (1983) who argued that H_2O is responsible for glass leaching for conditions in the pH range of 4–7:



In this model, molecular water enters the glass network, disassociates, and bonds with non-bridging oxygen sites to form silanol groups. As a result of charge compensation, the sodium ions become mobile and migrate to the surface of the glass along with hydroxyl co-ions (OH^-) (Hamilton and Pantano, 1997). There is only a one-to-one replacement of sodium with hydrogen atoms. However, the ratio of the two will always be greater than one since inflation of the ratio can occur as a result of subsequent water diffusion as the glass structure becomes less rigid.

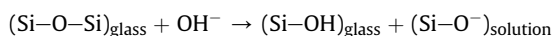
In the model of Smets and Lommen (1983) the exchange process for molecular water is determined by the number of available non-bridging oxygen sites (NBOs). Increasing the proportion of sodium (Na) to silica, for example, would accelerate the rate of molecular water diffusion by creating additional NBOs that open up the network and reduce glass connectivity. The impact of other network modifiers (e.g., CaO, MgO, K_2O , Li, Rb, Cs) depends on the strength of the cation charge and the size, or ionic radius. As a guiding rule, the lower the charge to ionic radius ratio, the more reactive the glass will be with water (Bunker, 1994).

In more complex soda-lime glasses where the number of network modifiers is greater the effect of each modifier on the rate of exchange OH^- with the alkali atom has not been fully quantified. However, Sinton and LaCourse (2001) indicate that the mechanism of exchange is still a two-stage process when in direct contact with aqueous media. In the first stage, there is an exchange at the surface between hydrogen and an alkali atom (R) that follows the reaction:



In a closed system as time proceeds, the depletion of alkalis and their transfer to solution, coupled with the increase in the

concentration of OH^- , raises the pH and breaks the Si–O–Si bonds of the glass matrix and causes the glass to dissolve:



In an open system where the moisture is water vapor, dissolution may be delayed or avoided over long exposure periods.

Developing a predictive model of glass durability involves an identification of the network modifiers that either accelerate or retard the first stage exchange process. Sinton and LaCourse (2001) have developed such a model to predict the rate of alkali exchange in a closed system for a fixed time at uniform temperature. Using the ISO static solution procedure (ISO 1985), crushed samples from twenty manufactured glasses were reacted with deionized water at 98 °C for 1 h. The leachate was analyzed by atomic absorption spectroscopy and step-wise regression analysis was used to quantify the relative effects of glass network modifiers on the exchange rate. The statistical analysis of the data set revealed that more durable glasses are those with low alkali content and a higher quantity of alumina. The addition of Na and K to the glass results in greater alkali exchange with Na^+ being preferentially leached out over the larger and slower moving K^+ . The presence of alkaline earths such as CaO and MgO were not statistically significant in terms of enhancing or reducing durability.

The work of Sinton and LaCourse (2001) indicates that the leaching of soda-lime-silicate glasses behaves in a predictable manner when exposed to solution and supports the goal of developing quantitative models to predict the leach rates for glasses of known composition. Archeological samples however, reside in open systems with a changing moisture environment and normally in vapor conditions where the relative humidity is less than 100 percent. Therefore, in this research we approach the problem of archeological glass hydration from the perspective of quantifying how much water (H_2O) enters the glass structure rather than attempting to quantify the amount of alkali removed from the glass matrix.

Research by Cummings et al. (1998) completed a series of vapor hydration experiments on a soda-lime-silicate glass containing network modifiers of CaO, K_2O , MgO, and Na_2O . In all exposures to water vapor at temperatures below 100 °C, nuclear reaction analysis of the hydrated surface layer indicated that the depth of hydration proceeded at the square root of time. Fern et al. (2006) provided additional evidence for the suitability of the $t^{1/2}$ rate model for water diffusion with depth in soda-lime glasses hydrated at room temperature. Interestingly enough, the fluctuations in the upper concentrations levels of their hydrogen profiles with time are suggestive of a dynamic period in the very early stages of hydration that is possibly indicative of a diffusion-glass relaxation process. This phenomena has been noted in hydrated silica glasses (Tomozaawa et al., 2001) and obsidian (Liritzis and Diakastamatiou, 2002; Brodkey and Liritzis, 2004; Stevenson and Novak, 2011) and is indicative of water diffusion complexity of in all forms of glass.

With this understanding, we have conducted a series of low temperature hydration experiments (<150 °C). We use secondary ion mass spectrometry (SIMS) and Fourier transform infrared spectroscopy (FTIR) to monitor the water diffusion and to determine if the water diffusion coefficients parallel the compositional effects on durability as determined from leaching experiments.

3. Glass composition

Two soda-lime glass fragments were selected from the fill deposits of an archeological site known as the Golden Ball Tavern (44PG439), Petersburg, Virginia. Constructed in the middle 18th century, and used as a tavern in the 1770s, the structure later

served as a private residence and commercial store of various types prior to being razed in the 1940s. Two types of glass were removed from the 18th century deposits at the site. Sample DHR-242 was a 4 mm thick slab of clear windowpane glass and DHR-243 was a 2 mm thick slab of the same form.

3.1. Bulk composition

The composition of each glass was determined by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) on a freshly polished surface (Table 1). Eight oxides were quantitatively determined. The glasses were very similar except that sample DHR-243 had approximately twice the amount of Al_2O_3 than DHR-242 (1.5% versus 0.7%). In addition, DHR-242 had a little over four times the amount of MgO than sample DHR-243 (0.81% vs. 0.19%) and 3.4% more SiO_2 . Analytical errors for the determinations were approximately 5% as determined from instrument calibration standards. A greater number and diversity of chemical compositions would have been desirable for experimentation, but this small sample is useful in that it will help direct and refine future experimentation.

3.2. Structural water

Water in manufactured glasses originates from the batch materials and the atmosphere during processing and is incorporated into the glass structure in the form of silanol groups ($\text{Si}-\text{OH}$). At concentrations of less than 1000 ppm, molecular water (H_2O) is not observed in manufactured glasses using infrared spectroscopy (Geotti-Bianchini and De Riu, 1995). It is important to know any pre-hydration contribution of structural water (OH) since bulk structural water concentrations can significantly influence the glass durability and diffusivity (Tomozawa et al., 2001). In addition, it is necessary to subtract the structural water from post-hydration water determinations to arrive at contributions originating only from surface hydration. The initial water concentration of each glass was determined by infrared spectroscopy using the recommended two-band procedure developed by Geotti-Bianchini et al. (1999) for water determinations in soda-lime-silica glass.

Infrared absorbance measurements were obtained from prepared thick sections on each glass composition. The sections were individually polished to remove the naturally hydrated surface using progressively finer grit polishing papers (180, 200, 400, 800, 1200) on a Buehler mini-met polisher. Spectra were obtained with a Bomem MB-120 spectrometer. A total of 150 scans were collected at an 8 cm^{-1} resolution using a 7 mm aperture plate. Two water bands were observed in the sample glasses. The first is a peak at 3523 cm^{-1} that represents weakly associated $\text{Si}-\text{OH}$ in the network cavities. The second water band is at 2918 cm^{-1} and represents $\text{Si}-\text{OH}$ units bonded with adjacent non-bridging oxygen atoms (Geotti-Bianchini and De Riu, 1995). The absorbance value at 4000 cm^{-1} is subtracted from the maximum heights of the water absorption bands to give an absolute measure of absorbance

independent of background conditions and the standardized values are summed. Calculation of the water concentration follows the equation:

$$C_{\text{H}_2\text{O}} = 1/d*(A_{3523} - A_{4000}/E_{3523}) + 4/3 (A_{2918} - A_{4000}/E_{2918})$$

Where: $C_{\text{H}_2\text{O}}$ is the concentration of water in mol $\text{H}_2\text{O}/\text{l}$ of glass, d is the thickness of the sample in cm, A is the infrared absorbance intensity, and E represents the extinction coefficients for the absorption bands. These latter values are $70\text{ l}/(\text{mol} * \text{cm})$ for the 3523 cm^{-1} band and $150\text{ l}/(\text{mol} * \text{cm})$ for the 2918 cm^{-1} band. The $4/3$ multiplier is a constant introduced by Geotti-Bianchini et al. (1999:105) to compensate for “the difficulty to measure directly the second bonded hydroxyl band”. The $C_{\text{H}_2\text{O}}$ value is converted to parts per million (ppm) units using the equation:

$$C_{\text{H}_2\text{O}}, \text{ ppm} = C_{\text{H}_2\text{O}} * 18000/Q$$

Where: 18,000 is a conversion constant (molecular weight of water $[18.0] * (\text{liters to grams conversion } [1000])$ and Q is the density of the glass in g/cm^3 . The densities of the sample glasses were determined by the Archimedes method in heavy liquid using a quartz standard with a density of $2.6688\text{ g}/\text{cm}^3$. These calculations resulted in initial (unhydrated) concentrations of 43 ppm for sample DHR-242 and 41 ppm for sample DHR-243 demonstrating an equivalency in structural water content.

4. Experimental vapor hydration

The windowpane fragments of each glass type were cut with a diamond blade trim saw into centimeter square sections for vapor hydration. The samples were then washed in demineralized water and allowed to air dry. In experiments under $100\text{ }^\circ\text{C}$, the hydration containers consisted of 125 ml polypropylene bottles. Each bottle contained one sample that was suspended by a Teflon thread over 10 ml of demineralized water. There was no contact between the sample and the water phase at the base of the bottle.

For experimental runs of $100\text{ }^\circ\text{C}$ through $140\text{ }^\circ\text{C}$ a durable one-liter polypropylene container was utilized. Two samples were suspended from sealed access ports on the lid over 50 ml of demineralized water. The accelerated hydration experiments were conducted between 60 and $140\text{ }^\circ\text{C}$. At $80\text{ }^\circ\text{C}$ samples were removed at approximately 10-day intervals with the longest sample exposure set at 90 days. Higher temperature runs at 100, 120 and $140\text{ }^\circ\text{C}$ were removed after a predetermined reaction period between 11 and 30 days in duration (Table 2, Table 3). All samples were hydrated in Precision convection ovens with a temperature variation of $\pm 1.0\text{ }^\circ\text{C}$. After each hydration period the samples were removed from the oven and allowed to cool to room temperature. This cooling process was accelerated by first opening the warm container and removing the samples. The specimens were then wiped with a soft tissue and allowed to air dry. As the samples were suspended over the container solution any minor dissolution of the polypropylene vessel would not impact the hydration process represented in the cooled sample.

Measurement of the surface absorbed water after $80\text{ }^\circ\text{C}$ experimental hydration was conducted by transmission FTIR in absorbance mode. A total of 100 scans were collected at 8 cm^{-1} resolution with a 7 mm aperture. The molecular water peak at 3523 cm^{-1} was monitored to assess the amount of H_2O that had diffused into the sample surface. Absorbance values were not converted to weight percent water concentrations because the values were suitable statistical analytical units. The 60– $140\text{ }^\circ\text{C}$ samples used in the activation energy analysis were run in

Table 1
LA-ICP-MS compositional analysis of two soda-lime glasses.

Oxide	DHR-242	DHR-243
Al_2O_3	0.7	1.5
CaO	13.5	17.6
Fe_2O_3	0.11	0.14
K_2O	0.11	0.15
MgO	0.81	0.19
MnO	0.004	0.008
Na_2O	10.56	9.47
SiO_2	74.02	70.62

Table 2

Reaction conditions and infrared absorbance (ABS) measurements for the LA/HM glass (DHR-242).

Lab no.	Temp° C	Days	Initial ABS	Hydrated ABS	Differential ABS
DHR-221	80	12.87	0.5245	0.5812	0.0567
DHR-222	80	20.00	0.5487	0.6200	0.0713
DHR-223	80	30.00	0.5551	0.6233	0.0682
DHR-224	80	40.98	0.5298	0.6211	0.0913
DHR-225	80	50.00	0.5740	0.6770	0.1030
DHR-226	80	60.00	0.5622	0.6690	0.1068
DHR-227	60	53.06	0.5436	0.7222 ^a	
DHR-226E	80	89.94	0.5622	0.8969 ^a	
DHR-228	100	30.00	0.5622	0.7395 ^a	
DHR-229	120	16.00	0.5436	0.7350 ^a	
DHR-230	140	11.09	0.5250	0.8239 ^a	

^a Analyzed by infrared transmittance.

transmittance mode using a Pike Technologies 30° reflectance accessory. This increased the absorbance intensity in these samples since the infrared beam was reflected back through the sample from a mirror placed on top of the sample. The isothermal 80 °C samples were also examined in reflectance mode to observe structural changes in the glass surface.

A selected number of hydrated surfaces from laboratory experiments (DHR-225, DHR-235) and from archeological context (DHR-294) were depth profiled using SIMS. The SIMS analysis was performed in order to find the point of inward water diffusion located at the full-width-half-maximum (FWHM) point on the hydrogen profile. The analyses were performed using a PHI Model 6300 quadrupole-based secondary ion mass spectrometer at Evans Analytical Group. A 5.0 KeV Cs⁺ primary ion beam with an impact angle of 60° with respect to surface normal was used and negative secondary ions were detected. Charge build up during profiling was compensated for by use of an electron beam. The measurements were performed using a 300u × 300u ion beam raster, which results in very little visual disruption to the sample surface. Generally, the SIMS depth scale accuracy is within 5–10 percent. This translates into an estimated error of ± 0.05u (Novak and Stevenson, 2012).

5. Analytical results

SIMS hydrogen profiles were obtained on two laboratory-hydrated samples to identify the type of interaction that occurred between the glass matrix and the surrounding water vapor. Samples DHR-225 and DHR-235 were hydrated under identical conditions at 80 °C for 50 days. In both cases, alkali depletion occurred at the surface of the glass but with very different results. The low alumina/high magnesium (LA/HM) glass (DHR-225) possessed a

Table 3

Reaction conditions and infrared absorbance (ABS) measurements for the HA/LM glass (DHR-243).

Lab no.	Temp° C	Days	Initial ABS	Hydrated ABS	Differential ABS
DHR-231	80	12.87	0.3071	0.3302	0.0231
DHR-232	80	20.00	0.3212	0.3536	0.0324
DHR-233	80	30.00	0.3356	0.3714	0.0358
DHR-234	80	40.98	0.3071	0.3441	0.0370
DHR-235	80	50.00	0.3212	0.3796	0.0584
DHR-236	80	60.00	0.3212	0.3796	0.0663
DHR-237	60	53.06	0.3212	0.2174 ^a	
DHR-236E	80	89.94	0.3212	0.7615 ^a	
DHR-238	100	30.00	0.3212	0.6192 ^a	
DHR-239	120	16.00	0.3212	0.6026 ^a	
DHR-240	140	11.09	0.3212	0.6159 ^a	

^a Analyzed by infrared transmittance.

well developed stepped hydrogen profile that penetrated to a depth of 0.9u at the FWHM point (Fig. 1). This was accompanied by a significant leaching of both Na and K that approximately corresponded to the FWHM point on the hydrogen profile. Si shows a slight depletion in the near surface region and Al is minimally enriched just below the surface.

In contrast, the high alumina/low magnesium (HA/LM) glass (DHR-235) exhibited minimal alkali depletion (Fig. 2). The hydrogen profile had an error function shape and it was in the first stages of developing a concentration plateau like DHR-225. The FWHM point of the profile occurred at approximately 0.1u and was 0.8u less than the LA/HM glass. The depletion of alkali at the surface had begun for both Na and K although it was much less pronounced than the LA/HM glass. Other constituents such as Si and Al were only very slight depleted from the bulk concentration level.

The high versus low rates of alkali depletion is mirrored by the water diffusion coefficients and activation energy constants generated from the FTIR absorbance values. The diffusion coefficients at 80 °C were calculated by a regression of the infrared absorbance values to the square root of time (LA/HM = 0.00019 Absorbance Units²/day; HA/LM = 0.000064 Absorbance Units²/day). Activation energy (*E*) values were computed from a regression of absorbance values against 1/*T* (Kelvin). An examination of the plot of absorbance intensity values with time (Fig. 3) indicates that H₂O diffuses into the LA/HM glass at nearly three times the rate as the more durable HA/LM glass. The lower activation energy for the LA/HM (Fig. 4) is 28,366 J/mol also reflects this fast reaction. The activation energy for the HA/LM glass (Fig. 5) is 38,571 J/mol and signifies that a higher energy threshold is necessary for water diffusion in this more durable and slower hydrating glass.

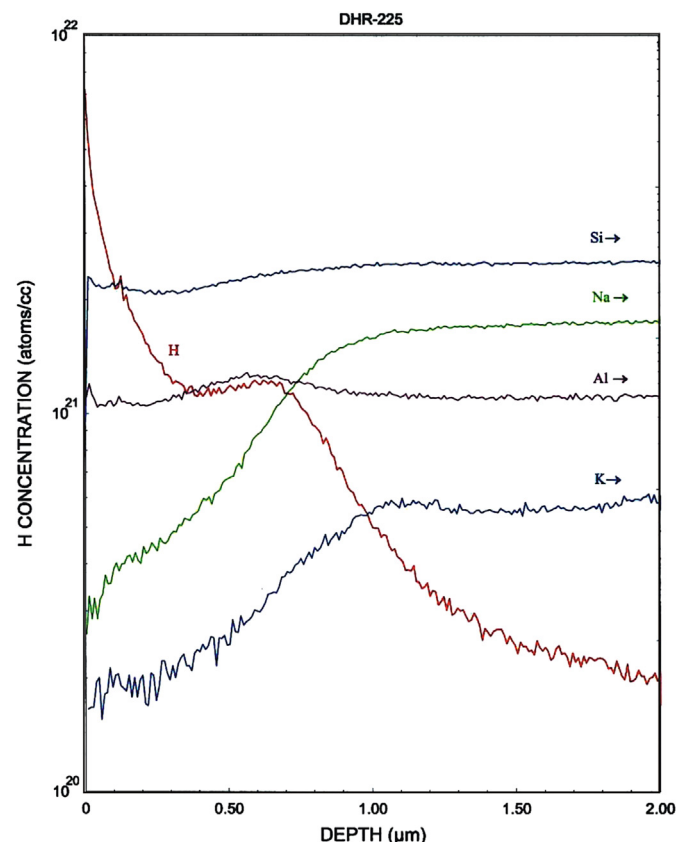


Fig. 1. SIMS profile of a hydrated (80 °C/50 days) LA/HM glass (DHR-225).

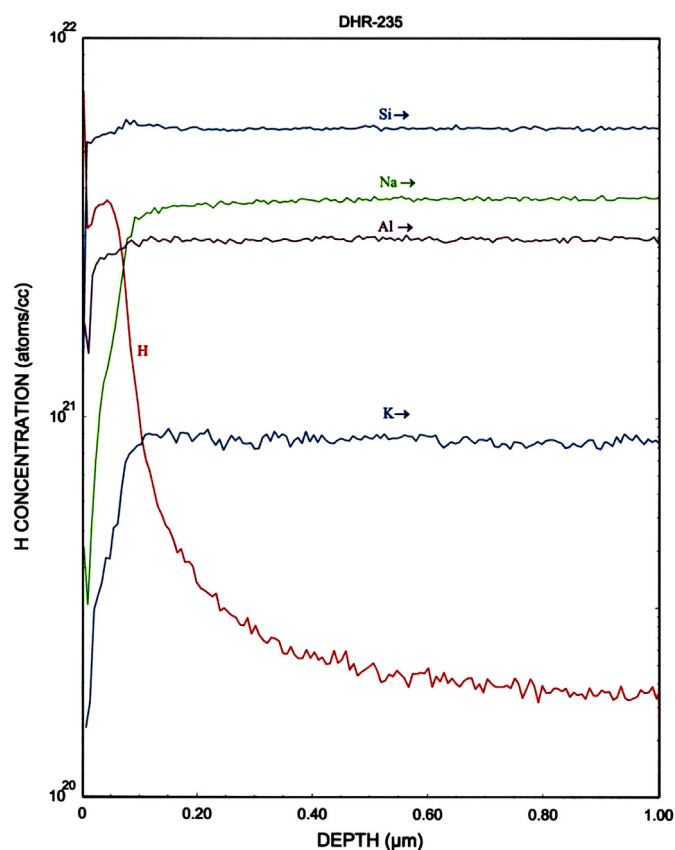


Fig. 2. SIMS profile of a hydrated (80 °C/50 days) HA/LM glass (DHR-235).

Infrared reflectance spectroscopy was used to monitor changes in the surface structure of the faster reacting LA/HM glass. The band at 1344 cm^{-1} represents the peak associated with the bridging oxygens and the band at 1255 cm^{-1} is associated with non-bridging oxygens (Fig. 6). With extended reaction at 80 °C the bridging oxygen peak remains stable but the peak associated with NBOs becomes smaller and finally quite degraded at 89.9 days. This degradation reflects the loss of modifiers to the glass structure as the sodium and potassium are selectively removed from the glass structure. To the far right of the spectrum at 975 cm^{-1} , there is the emergence over time of a significant peak that is noticeable at 20 days of hydration and afterward. This peak has been correlated with the Si–O stretching mode of the NBOs (Lee et al., 1997) and its growth parallels the loss of modifiers in the glass surface. Because of the higher durability and slower leaching rate, the HA/LM glass did not show a significant change in the silica bands over the same period of exposure to water vapor.

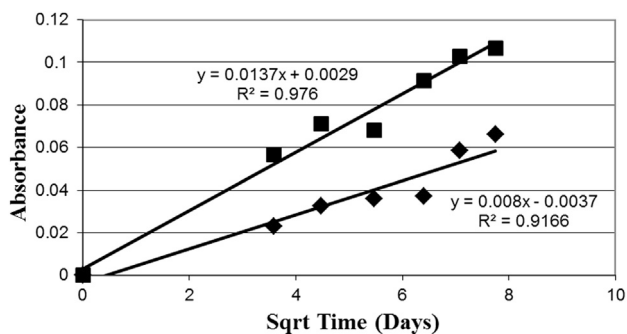


Fig. 3. Plots of infrared absorbance versus $t^{1/2}$ for the LA/HM glass (DHR-221/226; Upper line) and the HA/LM glass (DHR-231/236; Lower line).

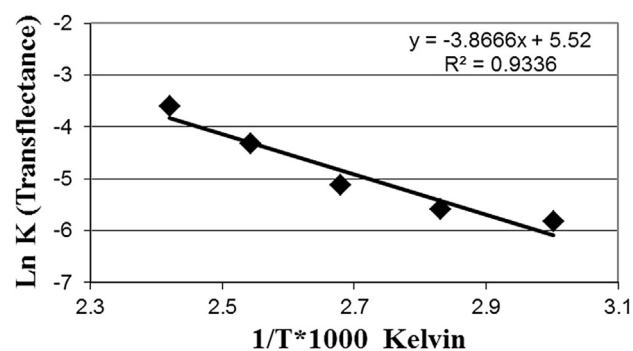


Fig. 4. Activation energy plot for LA/HM glass (DHR-226E/230).

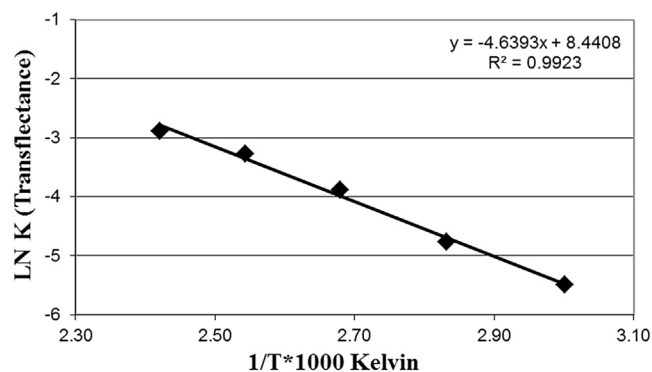


Fig. 5. Activation energy plot for HA/LM glass (DHR-236E/240).

An additional SIMS profile was obtained from the fracture surface on an archeological specimen (DHR-294) from a slave quarters on Mulberry Row known as Building “O” at Thomas Jefferson’s home in Virginia, Monticello. The structure was destroyed around

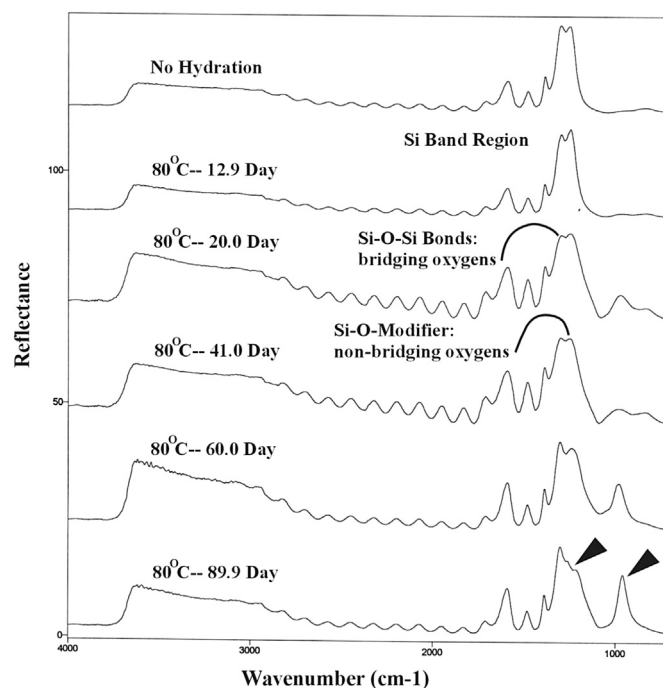


Fig. 6. Infrared reflectance spectra of the LA/HM glass (DHR-242) hydrated at 80 °C for 12.9–89.9 days. Black arrows point to the degraded 1255 cm^{-1} and emerging 975 cm^{-1} infrared bands.

AD 1840. This profile was obtained in order to assess the degree of similarity for hydrogen and alkali profiles between laboratory and archeological specimens since previous studies show that archeological sites can be complex chemical environments (Romich, 2003).

Sample DHR-294 is lower in bulk Al and Na (Fig. 7) compared to both laboratory samples based upon the atoms/cc values on the SIMS profiles (Figs. 1 and 2). It is also a low durability glass and exhibits a hydrogen profile very similar to the LA/HM laboratory specimen (DHR-225). Hydrogen has diffused at the FWHM point to a depth of approximately 0.7μ and alkali depletion of Na and K begins near this same point. SiO_2 exhibits a slight near surface depletion. However, Fe_2O_3 and Al_2O_3 are greatly enriched within the hydrated layer. The iron may originate from the soil, which may have been added by the decomposition of building nails and other metal artifacts within the soil fill. We are not sure at this time why Al_2O_3 exhibits such a pronounced surface enrichment.

6. Discussion

Secondary ion mass spectrometry and infrared spectroscopy have been used to show that an alkali exchange reaction occurred in the low temperature vapor hydrated glasses. Infrared absorbance measurements on a time series of hydrated samples indicated that the amount of total water diffused into the surface followed a square root of time dependence and confirmed the conclusions of previous studies using other analytical procedures for tracking the depth of diffused water.

Also important was the observation that the rate of molecular water diffusion varies in response to the concentration of alumina

contained within the glass matrix. The remaining constituent oxides in the glass exhibit only modest variability. If magnesium has little effect, as demonstrated previously (Sinton and LaCourse, 2001), then alumina appears to be a key variable in determining the rate of surface water diffusion even at very low concentrations (Wassick et al., 1983). The higher alumina glass in this study exhibited a much lower diffusion coefficient and higher activation energy than the low alumina glass hydrated under the same conditions. These data suggest that a predictive model for estimating water diffusion coefficients and activation energies in some types of soda-lime-silica glass could be developed with relatively few parameters but a much wider range of glass compositions should be evaluated to establish clear dependencies.

The SIMS hydrogen profiles obtained in this analysis were very informative about cation exchange. Profiles of this type are frequently used in obsidian hydration dating (Liritzis and Laskaris, 2012) but they have two features that make their use for archeological dating of manufactured glasses uncertain. First, the leading edge of each laboratory hydrated hydrogen profile has a progressively declining slope that extends well beyond the FWHM point (Figs. 1, 2, 7). This may be due to a deeper cation exchange process or it could be related to a surface roughness of the sample that lowers the resolution of the secondary ion profiling process (Novak and Stevenson, 2012). This surface roughness may come from leaching that creates micro-voids in the surface of the hydrated glass. For archeological materials, alkaline attack in soils of higher pH (>7) may also cause roughness, as will sediment abrasion or trampling while in archaeological context. Secondly, water concentration, or height of the hydrogen profile, is a result of the combined leaching and molecular water diffusion involving multiple cations which does not produce a stepped profile with a near-linear plateau (Fig. 7). This is a requirement for the SIMS-SS dating method that is not met by this material and the archeological conditions that it has experienced.

The SIMS profile recovered from the archeological sample does point to some potential problems connected with future implementations of soda-lime glass dating using infrared sampling methods. Most noticeable is the depletion of silica at the surface of the artifact that may have been lost through dissolution by ground water at the archeological site (Fig. 7). This loss of depleted glass at the surface, and the low hydrogen concentration in the near surface region, means that the full hydration history of the glass has not been retained. Therefore, it will be necessary to demonstrate that artifact structural integrity has not been compromised prior to any attempts at dating with laboratory developed diffusion coefficients. A potential solution to this problem would be to first monitor the diminishing 1255 cm^{-1} infrared band and the emerging infrared band at 975 cm^{-1} which reflect the extent of alkali depletion from the glass structure. Couple this with a comparison of the Si–OH band at 1344 cm^{-1} in the altered region and the same band on a polished surface of the same artifact. An equivalency of band shape and intensity would signify artifact structural integrity.

7. Conclusions

In this set of preliminary experiments the objective was to determine if water diffusion in soda-lime-silicate glass behaved in a predictable manner dependent upon time, temperature and composition. If water diffusion coefficients varied predictably based upon glass chemistry this would provide guidance for additional accelerated hydration experiments that could be used to develop a dating method for this glass type. Two historic manufactured glasses, differing principally in their alumina and magnesium content were selected for accelerated vapor hydration to determine if the rate of surface water diffusion paralleled the

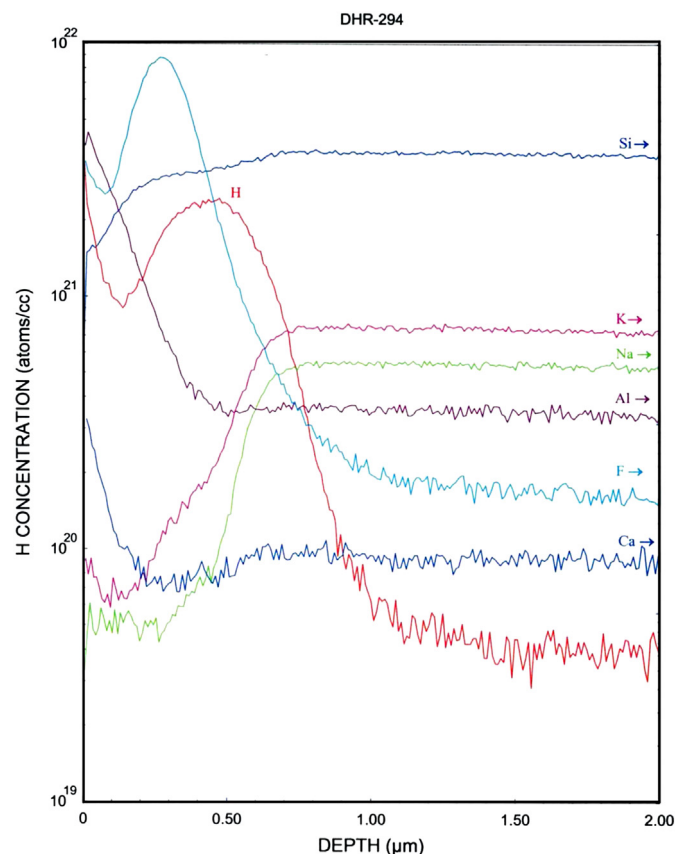


Fig. 7. SIMS profile of a hydrated low alumina archaeological glass (DHR-294) from Building "O", Monticello.

results of glass leaching studies on similar glass. These studies have shown that alumina is an influential component that reduces the number of non-bridging oxygen sites which slows the overall rate of alkali depletion and may correlate with water diffusion coefficients for soda-lime glasses.

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